Study on the Kinetics of Geopolymerization

by

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14372

Dissertation submitted in partial fulfilment of

the requirements for the

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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(CHEMICAL)

Approved by,

_____

(Prof. Dr. Khairun Azizi binti Azizli)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
September 2014

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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(MOHAMAD MUHAIMI BIN IBRAHIM)

ABSTRACT

Geopolymer is defined as the chains or networks of mineral molecules synthesized by a reaction of aluminosilicate mineral with alkali activator solution. It possesses good chemical and mechanical properties and has a great potential to be used in various application. The aim of this research is to conduct a study on the kinetics of geopolymerization by applying Avrami's kinetics theory. The study focused on the effect of curing temperature and concentration of sodium hydroxide (NaOH) solution on geopolymerization. Setting time of fresh pastes and compressive strength of hardened pastes were determined using vicat needle test and compression machine respectively. Chemical dissolution method was used to determine the degree of reaction on hardened pastes. The samples were tested at different age of curing period which were 1, 7 and 24 hours. Avrami's kinetics theory was applied to analyze the geopolymerization profile. Based on the kinetics study, the growth rate (K) slightly increased from 0.51 to 0.54 and crystall shape (n) value slightly decreased from 0.472 to 0.460 with the increased in NaOH concentration from 8 M to 10 M. As the curing temperature was increased from 60 to 80°C, K decreased from 0.258 to 0.237 and n increased from 0.152 to 0.460. Higher n value indicated better crystall formation. While lower K value indicated the reaction rate is faster which resulted in geopolymer with better properties.

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CHAPTER 1 : INTRODUCTION

1.1 Background Study

Geopolymers are a class of cementitious aluminosilicate binder materials synthesized by a geopolymerization reaction of aluminosilicate minerals such as industrial solid wastes, calcined clays, and natural minerals with alkali activator solutions at ambient or higher temperature (Davidovits, 1991). They have been gradually deemed to be potentially revolutionary materials in recent years for the great advantages, such as preparation of zeolites, using in replacements of traditional Portland cement, superior thermal and chemical resistance properties as well as a potential value in stabilizing radioactive and toxic wastes (Zhang et al., 2008).

At present, the influencing factors of different Si/Al ratios, amount of water, concentration and variety (Na+, K+, Cs+) of alkali cations have been investigated on the mechanical properties, phase transitions, microstructural development of geopolymers or geopolymerization (Zhang et al., 2010). Curing condition during the initial stage of geopolymerization reaction is one of the important factor affecting the rate of formation and quality of the geopolymer. More recently, researchers are using experimental skills and theoretical techniques to understand the kineticss of geopolymers formation. The gels formed usually were characterized by chemical analysis, FT-IR spectroscopy, X-ray diffraction or MAS-NMR. The conclusion for all the discussion is that geopolymerization involves a complex multiphase process.

According to Hanie (2012), the growth rate (K) increased with the concentration of solution and temperature and Avrami exponent (*n*) trend was increasing as growth rate increases and vice versa. The parameter used in the Avrami's theory is the volume fraction of crystalline area determined by using Leatherhead Food Research Analyzer (LFRA). Avrami's theory concept is more understandable by observing raindrops falling

in a lake. The circle of waves expansion are the growth, and the points of impact are the nuclei of crystall (Ismail et al., 2008).

Results revealed by Arioz et al., (2012), mentioned that the degree of reaction increased with increasing molarity. Unreacted fly ash is determine by using 3 mol HCl to dissolve CaO and MgO from hardened geopolymer. Na_2CO_3 is employed to remove SiO_2, Al_2O3 and Fe_2O_3. According to Rattanasak et al., (2010), incorporation of admixtures in geopolymer result in higher degrees of reaction and consistent with the results of compressive strength.

Most of the research mentioned above was primarily focused on the the kineticss models as well as studying mechanical characteristics. The main purpose of this study is to investigate the effect of synthesis parameters, curing temperature and alkaline concentration on geopolymerization. Simultaneously the characteristic, compressive strength and setting time are determined.

1.2 Problem Statement

Researches were well-documented to explain the effect of proper mix design on the compressive strength of geopolymeric materials. However, the underlying mechanisms controlling geopolymer formation and alkali activation in general are not well understood. Most studies related to geopolymer are based on its chemical and physical properties after setting time such as compressive strength, acid resistance, water penetrability and stability of geopolymer (Hanie et al., 2012). However, there are only a few researches were conducted to investigate the effect of synthesis parameters especially at the curing phase. Therefore, this research is focusing more to the the effect of different concentrations of alkaline solution as well as effect of different curing temperature on the geopolymerization. The Avrami's theory will be used to explain the kinetics of geopolymerization based on the crytall shape (n) and growth rate (K). Subsequently, solidification period and compressive strength of geopolymers are tested.

1.3 Objectives

The aim for this project is to conduct a study on the kinetics of crystallization of geopolymer by varying different synthesis parameters. The kinetics of geopolymerization will be analyzed by using Avrami Kinetics Theory.

- To prepare and determine fly ash based geopolymer properties by varying NaOH concentration and curing temperature.
- To study the effect of curing temperature and NaOH concentration on kinetics of geopolymerization by determining the cystall shape (n) and growth rate (K) using Avrami's Theory

1.4 Scope of Study

The scope of this study consists of characterizations and synthesis parameters of geopolymerization. Firstly, the characteristics of the fly ash is determined and subsequently the geopolymer in order to determine the relationship between the composition of raw material and the properties of the fly ash-based geopolymer. The concentration of NaOH and curing temperature are prepared at concentration of 8 M and 10 M. The curing temperature is set at 60 ºC and 80 ºC respectively. Geopolymers are cured for 1, 7, and 24 hours to study the kinetics of geopolymerization within 24 hours. For fresh paste geopolymer, the setting time is determined whilst the cured paste geopolymer is tested for compressive strength by using compression machine. Chemical dissolution method is used to determine the mass of unreacted fly ash to calculate degree of reaction. Degree of reaction values are used to study the kineticss of geopolymerization by using Avrami Theory.

CHAPTER 2 : LITERATURE REVIEW

2.1 Geopolymers

2.1.1 Terminology and Chemistry

Geopolymer was described as a group of mineral binder with chemical composition similar to natural zeolitic materials but with amorphous microstructure It was introduced by Davidovits in 1978. Another term suggested was poly(sialate) for the designation of geopolymers based on silico-aluminate (Wallah and Rangan, 2006). The chain and ring of polymers with Si^{4+} and AL^{3+} with oxygen are known as polysialate. Polysialate emperical formula is:

$$M_n(-(SiO_2)_z - AlO_2)_n . wH_2O$$

where,

z = 1,2,..,32

M = monovalent cation

n = degree of polycondensation

According to Davidovits, (1999), 3 types of polysialates were distinguished as shown in Figure 2.1.

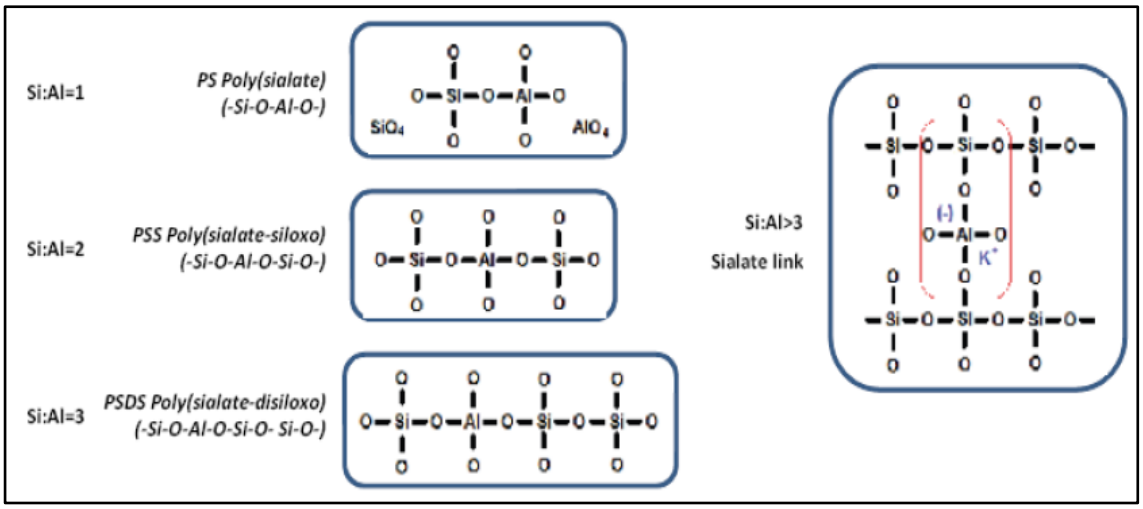

Figure 2.1 Geopolymer Terminology (Davidovits, 1999)

Figure 2.2 represents chemical reaction of alumino-silicate oxides (Si_2O_2, Al_2O_2) with alkali polysilicates to form polymeric Si-O-Al bonds involves in Geopolymerization (Wallah and Rangan, 2006).

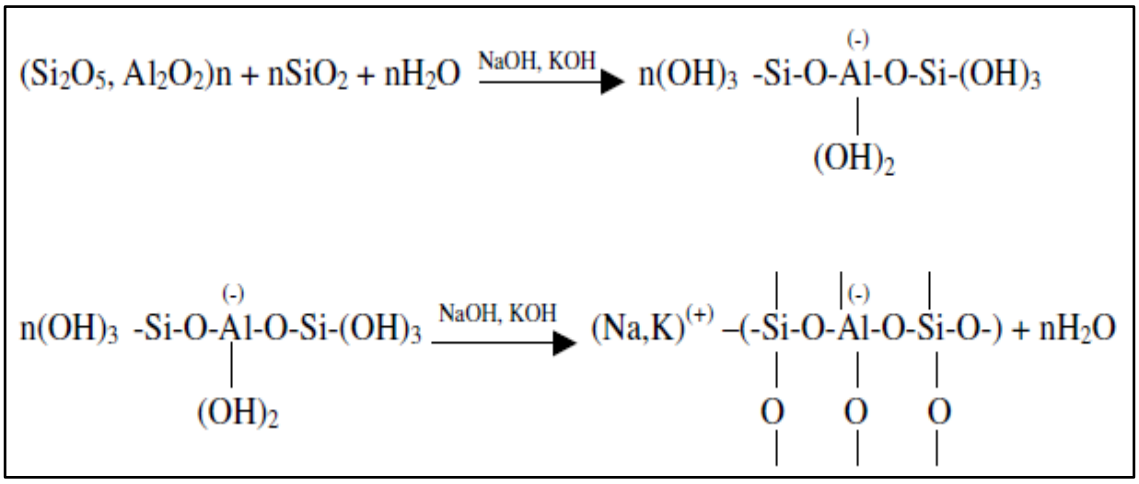

Figure 2.2 Chemical Reaction of Geopolymer (Wallah and Rangan, 2006)

Polycondensation of silica and alumina precursors and high alkali content is been utilized to achieve properties. It makes geopolymers known as alkali-activated as well. The expression alkali-activated could not be used as its more to represent a harmful property well known in concrete which is alkaline-aggregate reaction (AAR), (Wallah

and Rangan, 2006). During the curing process, water produced from the chemical reaction of geopolymers formation is removed from the mixture.

2.1.2 Raw Materials

Raw materials play an important role in the formation of geopolymer. Primarily, kaolinite and metakaolin are used as sources of alumina silicate to synthesis geopolymer. Compared to kaolinite, metakaolin has higher reaction activation which can be derived from kaolinite which is a kind of artificial pozzolanic material. According to Xu and Deventer (2000), any pozzolanic compound or source of silica and alumina that is readily dissolved in the alkaline solution acts as a source of geopolymer precursor species and thus lends itself to geopolymerization.

In recent years, the use of natural minerals and industrial wastes such as fly ash, slag and waste glass were also investigated as sources of raw materials for geopolymerization. Fly ash, which could cause serious environmental problems is the main solid waste generated from coal-fired power stations (Figure 2.3). Therefore, it is comparatively used in the industry extensively. As for insufficient Al dissolution, the addition of kaolinite is necessary to produce a gel of desired composition (Xu and Van Deventer, 2000). However, kaolinite added in excess will not react since it may not take part in the synthesis at all (Van Jaarsveld et al.,2007).

Figure 2.3 Source materials of geopolymer (Geopolymer Institute)

Besides that, mechanical strength can be improved by using metakaolin due to decrement of water and salt transportation in the final product (Kostas et al.,2007). In this study, fly ash is used as the source of Alumina (Al) and Silica (Si) to produce geopolymer. In recent study, Palm Oil Fuel Ash (POFA), a by-product when palm oil husks and palm oil shells are burned in the boiler of palm oil mill is been blended with fly ash to enhance geopolymer properties (Figure 2.4).

Figure 2.4 Palm Oil Fuel Ash (POFA) (Azrif, 2011)

2.1.3 Activator Solution

Geopolymer liquor was defined as an alkali hydroxide which is required to dissolve the raw material whereas sodium or potassium silicate solution functions as a binder, alkali activator and dispersant or plasticiser. The alkali component includes the element of the first group in the periodic table which is also knows as alkali activated alumina-silicate binders or alkali activated cementitious material.

A study by Hardjito et al. (2004) concluded that strong alkalis are required to activate the silicon and aluminium present in fly ash and setting additives in order to allow the transformation of glassy structure either partially or totally into a very compacted composite. In theory, any alkali and alkali earth cation can be used as the alkali element in geopolymerization reaction. But most of the studies have focused on the effect of potassium and sodium ions (Kostas et al., 2007). In addition, NaOH, Na_2SO_4, water-glass, Na_2CO_3, K_2CO_3, KOH, K_2SO_4 or a little amount of cement clinker (Xiong et al., 2004).

There many factors need to be considered in choosing the type of alkali metal during geopolymer synthesis. One of the most important influence is the type of source material as well as the application purpose of the resultant geopolymers (Van Jaarsveld, 2007). For instance, sodium silicate has been used for more than a century for the production of commercial products such as special cements, coatings, mouldedarticles and catalysts. He also added that the alkali metal cations control and affect almost all stages of geopolymerization especially during gel hardening and crystal formation since it contributes to the structure formation of geopolymers.

2.1.3 Properties of Geopolymer

Geopolymers were reported to possess good chemical and physical properties and could possibly used in various application. Geopolymer can rapidly harden at room

temperature depending on the mix design and condition during the manufacturing process.

2.1.3.1 Compressive Strength

Chemical reaction of the geopolymer gel is due to substancially fast polymerization process (Hardjito et al., 2004). It was observed that the age of the concrete did not vary its compressive strength. In term of OPC, it go through hydration and strength is increasing with time.

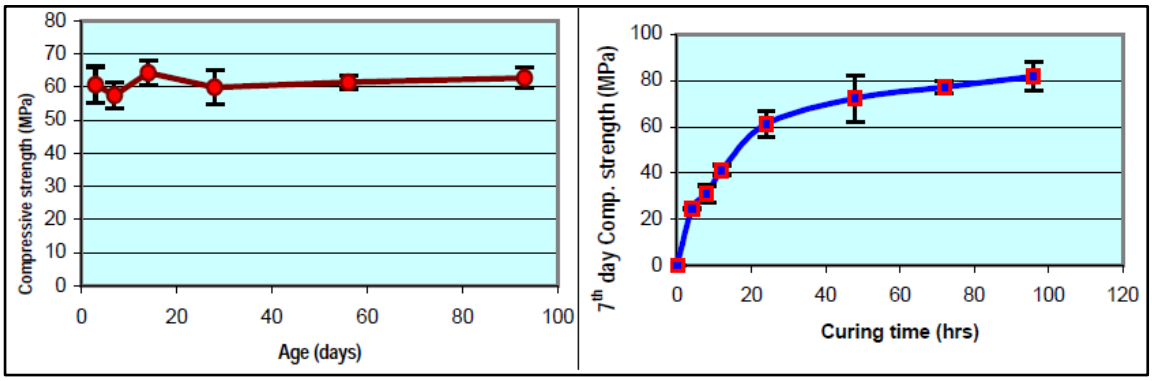

Figure 2.5 Compressive strength over time (Hardjito et al., 2004)

Figure 2.5 shows that the increment rate of compressive strength is high only during early stage of curing period. According to Hardjito et al., (2004) the compressive strength of geopolymer is in the range of 20 MPa after only 4 hours at 20 ℃. After 28 days, 70-100 MPa was achieved.

Compressive strength of geopolymer is also affected by variation of the amount of alkaline activator. Increasing the activator content does not necessarily improve the strength (Nath et al., 2012). The 28 day compressive strength of mixtures showed decrement with the increase of alkaline liquid content from 35% to 45%. This is due to higher water to solids ratio of the mixtures cause high liquid content.

The development of compressive strength over time due to sodium silicate/sodium hydroxide was also been investigated preiviously. However, the 28-day compressive strength of geopolymer mortar and concrete mixture did not show significant variation with the variation of Sodium Silicate/Sodium Hydroxide ratio in the range of 1.5 to 2.5 (Nath et al, 2012).

2.1.3.2 Setting Time

Setting time shows gradual reduction as higher solid to liquid ratio are used. Water content influenced setting time in the initial mixture. High reaction rate in greater solid to liquid ratio fasten the setting time of geopolymer. He also reported that the addition of POFA reduced the setting time. Reported in previous research, iron rich material particles inhibit the dissolution of alumina-silicate during geopolymerization.

Activator liquid content also affected the setting time of the mixture. This is due to the change in reaction rate as the activator content is changed. According to Nath et al., (2012), an increasing trend of both initial and final setting time were observed with increasing alkaline liquid content.

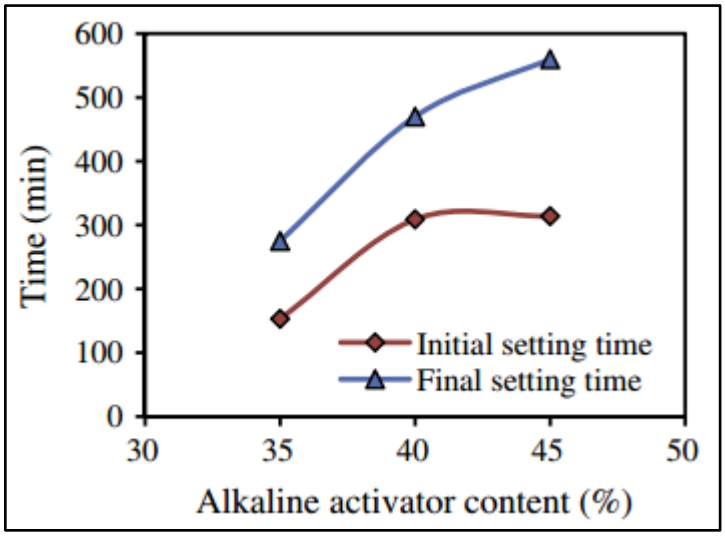

Figure 2.6 Effect of the amount of alkaline liquid on setting time (Nath et al., 2012)

Increment from 35% to 40% doubled the initial setting time while increment from 40% to 45% showed no significant increase (Figure 2.6)

2.1.4 Applications of Geopolymeric Materials

According to Davidovits (1984), geopolymeric materials have a wide range of applications in the field of industries such as in the automobile and aerospace, nonferrous foundries and metallurgy, civil engineering and plastic industries. The type of application of geopolymeric materials is determined by the chemical structure in terms of the atomic ratio Si:Al in the polysialate. Davidovits (1999) classified the type of application according to the Si:Al ratio. Range of Si:Al between 1 to 3 generates a very rigid network, while a polymeric characteristic is produced with ratio more than 15.

Geopolymers have similar chemical properties as zeolitic materials. The properties have been known and proven for their effectiveness in toxic waste management. The ability to absorb the toxic chemical wastes is proven in previous study by Davidovits (1984). An overview and useful test results is provided by Comrie et. al.,(1988) on the potential uses of the geopolymer in toxic waste management. It was recommended that the geopolymeric materials is applicable for waste containment. A product, GEOPOLYMITE, a type of geopolymeric binder is a registered trademark of Cordi-Geopolymere SA. It was prepared from a mixture of various aluminasilicates with alkali activators.

Geopolymer is also applicable in the strengthening concrete structural elements. Instead of organic polymers, geopolymer is used to fasten carbon fabrics to concrete beams have been tested. Results reported that geopolymer provided more adhesion bond to both surface of concrete and fabrics inter-laminar. Plus, fire resistant characteristic of geopolymer was observed and it did not degrade under UV light. The chemical properties of geopolymer are compatible to concrete.

While in Australia, geopolymer has been used in developing many industries. For example in sewer pipeline products, railway sleepers, building products including fire and chemically resistant wall panels, masonry units, protective coatings and repairs materials, shotcrete and high performance fibre reinforced laminates. The other suitable applications been studied is simplified in Table 2.1.

Table 2. 1 Application of Geopolymer

Classes	Applications
Construction (Geopolymer Institute, 2010)	-Bricks -Ceramics -Low CO_2 cements and concretes
Industrial (Geopolymer Institute, 2012)	-Fire protection for structures -Sealants for industry, 200 to 600 ℃ -Radioactive and toxic waste encapsulation
Process (Geopolymer Institute, 2012)	-Fire protection fibre glass composite -Heat resistant composites, 200 to 1000 ℃
Manufacturing (Geopolymer Institute, 2011)	-Tooling for aeronautics Superplastically formed (SPF) aluminium -Foundry equipments

2.2 Synthesis Parameters

The quality of geopolymer is influenced by the control of parameters during synthesis process. For instance, high compressive strength of geopolymer can be produced by using high reactivity source material (Alonso and Palomo, 2001). The factor that affect unconfined compressive strength was presented by a study conducted by Divya et al., (2007) ; curing temperature, curing time, silicate and hydroxide ratio, alkaline concentration and pH.

In this study, the compressive strength of geopolymer is used to study the kinetics of geopolymerization by using Avrami Theory. Thus, two parameters is chosen to deepen the understanding of geopolymerization ; curing temperature and concentration of alkaline solution.

2.2.1 Solid/Liquid Ratio

Solid/liquid ratio of the starting materials determines the water content in geopolymeric matrices. Divya et al., (2007), stated that the strength increases as the ratio of geopolymer solid-to-water by mass increases. The trend is similar to cement-to-water ratio in the compressive strength of Ordinary Portland Cement (OPC) even though their chemical processes involved in the formation of binders are differed.

It has been proven that by reducing water content in the aqueous phase of synthesis process could affect all stages of geopolymerization process positively. However, insufficient wetting may be the result of continuous decreasing of water content. This could negatively affect the formation of geopolymer.

The higher solid-to-liquid ratio will result in faster setting time due to increase of reaction rate (Zhang et al., 2009).It can be concluded that higher solid/liquid ratio has higher polycondensation rate since higher water content accelerate the reaction. Nevertheless, the dilution effects of geopolymer could be reduced if too much water is used.

2.2.2 SiO_2/ Al_2O_3 Ratio

In general, the polycondensation of hydrolyzed aluminate and silicate species is believed to be the main contributor towards hardening process of geopolymer. Depending on the concentration of Si in the mixture, condensation between aluminate and silicate or between silicate species themselves are expected to occur. De Silva et al., (2007) reported the effect of initial Si/Al ratio on the setting based on metakaolin since it is a good source of Al_2O_3 and SiO_2 which is highly reactive with alkaline activators.

The compressive strength increased as the SiO_2/ Al_2O_3 ratio increased (Smith et al., 2010). When the ratio reached about 10, compressive strength development became

slower and dropped as the ratio is beyond 15.9. As the ratio is greater than 8, the mixtures turned to be sticky and difficult to pour into mold. According to Fletcher et al., (2005), the compressive strength is reported to increase as the ratio of $SiO_2/\ Al_2O_3$ increased. The failure mode changed from crushing to deformation and compressive strength reduced beyond the ratio of 16.

2.2.3 Alkaline Concentration

Reaction between aluminosilicate with highly concentrated aqueous alkali hydroxide or silicate solution will produce the geopolymer (Nugteren et al., 2008). According to Hardjito (2004), the alkaline concentration is varies and usually between from 8M to 16M. He found that if the sodium hydroxide concentration in molar is high, it will result the higher compressive strength. It is observed that the strength characteristic of geopolymer concrete is influenced by the concentration of sodium hydroxide (Anuar et al, 2011). Type and concentration of alkaline solution affect the dissolution of fly ash. Rattanasak et al.,(2009) found the result of measuring the silica and alumina ion at different concentration of alkaline.

They also observed the surface of fly ash before and after leaching with different concentration of Sodium Hydroxide.

Figure 2.7(a) represents the smooth original surface of fly ash. After going through 10 minutes leaching in Sodium Hydroxide, the surface becomes rough depending on the concentration of Sodium Hydroxide. Based on Figure 2.7 (b), (c) and (d), the less sign of attack is show at 5M of Sodium Hydroxide as compared to 10M and 15M of Sodium Hydroxide.

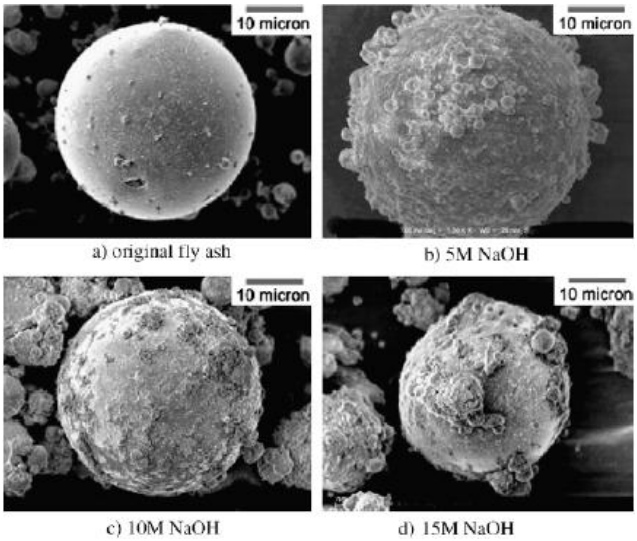

Figure 2.7 Microsurface of fly ash (Anuar et al, 2011)

2.2.4 Curing Temperature

Curing temperature effects on geopolymer properties has been thoroughly studied in previous researches. The initial and final setting time for room temperature and 60°C shall be observed and the Figure 2.8 obviously show that geopolymer at setting time 60°C is faster that at the room temperature. This is due to water loss increasing the setting rate. It shows that at room temperature, the time taken for the geopolymer to reach final setting is about 9.5 hours (Wang and Cheng, 2008).

Another study conducted by Bing-hui et al., (2014) on the effect of curing temperature on electrical conductivity in geopolymerization process where it is concluded that curing at 60 ºC gives the best mechanical properties and compressive strength.

Based on the graph, the highest compressive strength was achieved by specimen cured at 80 ºC for 20 minutes and above that.

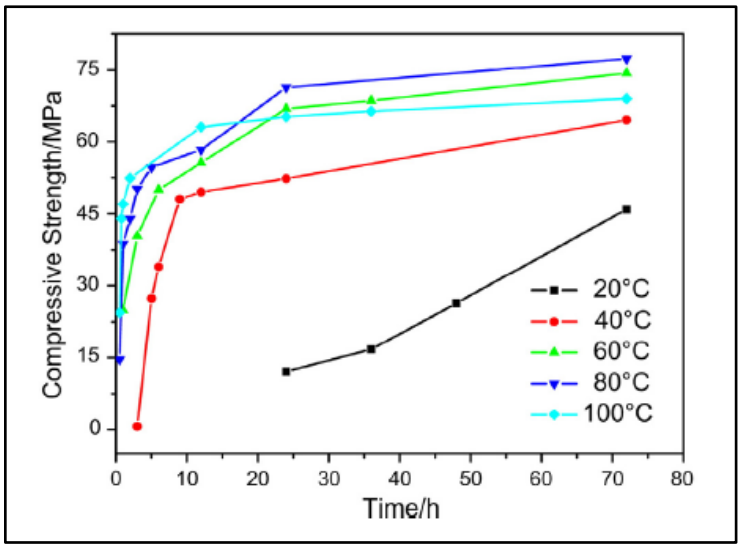

Figure 2.8 Influence of curing temperature on compressive strength (Bing-hui et al., 2014)

2.2.5 Curing Time

The effect of curing system on properties of geopolymer has been studied recently. Fly ash based geopolymer bricks showed that the curing system have a significant effect to its properties. Geopolymerization reaction is accelerated as the curing time is prolonged and resulted in higher compressive strength. In the research, highest compressive strength is recorded by the sample cured at 70 °C for 24 hours.

Fared et al., (2011) found that by varying curing time in range of 24-96 hours, the results indicates that longer curing time give higher compressive strength. Curing time plays important role in geopolymerization because the water content is needed in reactions. Manesh et al., (2012) carried out an experiment on the effect of duration and temperature on compressive strength of geopolymer. They cured all specimens in an oven at different range of temperature for 6, 12, 16, 20 and 24 hours duration. It is observed that increased in duration and temperature produced specimen with higher compressive strength.

2.3 Crystallization Theory

2.3.1 Avrami's Law

Avrami's law has been developed by Avrami, Johnson and Melh about 70 years ago and been expressed in exponential form. The law was primarily derived to explain the allotropic phase transformation in solid. Avrami's law is currently applicable to many applications. For example, crystallization of polymers, heat treatment in industry and thermal decomposition of solid.

Two processes which are nucleation and the growth are the main basis of Avrami;s model. The growth represents the increase in the size of the nuclei into the initial phase during time (Govin et al., 2013). Although Avrami introduce his model for describing the kineticss of first order phase transition for a three dimensional environment, subsequently his approach has been successfully applied even for transformation occurring at solid (Fanfoni and Tomellini (1996).

2.3.1.1 Application of Avrami's Law

Avrami's theory is an extremely simple approximation proposed years ago. It is widely used to analyse metastable decay in fields ranging from metallurgy to food science. The theory appears to give reasonable results, even when its restrictive assumptions are not well satisfied. Some of application in previous research are summarized in Table 2.2.

2.3.1.2 Application of Avrami's Theory in Crystallization

Kinetic of phase change is formulated with the experimental support. The assumptions made that the germ nuclei of new phase nucleated by existing germ nuclei in the old phase. Some of the nuclei is activated to transform into new phase growth nuclei. The process thinning the density of germ nuclei. It is also diminished as the germs nuclei is

consumed by the growing grains nuclei. The relation of nuclei and transformed volume is quantitatively expressed in time scale for any substance and process.

Table 2. 2 Application of Avrami's theory

Application	Justification
Kinetics modeling of Colonization of mortar surface by alga (Govin et al., 2013)	Collonization rate follows a sigmoidal curve for the surface fraction colonized as function of time. Avrami's model considered the alga spots as nuclei which are very small and randomly distributed on the surface. By using Avrami's model, the colonization mechanism can be modelized.
Kinetics approach for describing Volmer Weber growth mode at solid surface (Fanfoni and Tomellini, 1996)	A model is presented to describe time dependence of photoelectron and/or Auger signals during the overlayer formation in case of Volmer Weber growth mode.
Kinetics of the wax crystallization (Ismail et al., 2008)	A solid layer formed by precipitating wax deposits on the inner tube reduces flow rates. The study on the kinetics using Avrami's theory enhance the control of the wax formation to increase flow effeciency.

Heuristic Avrami phase transition theory is a well known description of crystallization kineticss. Melvin Avrami, who adapted the formulations intended for metallurgy to the needs of polymer crystallization. The original derivations were simplified by Evans and rearranged for polymer crystallization by Meares and Hay (Yang et al., 2005). For the bulk crystallization kineticss can be represented as

$$\mathbf{1} - \boldsymbol{X} = \boldsymbol{e}^{-\boldsymbol{V_t}}, \quad \text{.....(Eq 2.1)}$$

where $\boldsymbol{X}$ is the degree of crystallization and $-\boldsymbol{V_t}$ is the volume of crystallization material. Two cases should be considered to determine the unknown.

a) the nuclei are predetermined, that is, they all develop at once on cooling the polymer

b) the crystalls nucleate sporadically

For case (a),

$$dV_t = 4\pi r^2 L dr,$$ ..... (Eq 2.2)

where r is the radius of the spherical crystal at time t, L is the number of nuclei. The radius is been assumed to grow linearly with time, $r = \kappa t$. Integrated equation 2.2 is substituted into equation 2.1, one obtains,

$$1 - X = e^{-Kt^3},$$ ..... (Eq 2.3)

where the growth rate, $K = \frac{4}{3}\pi\kappa^3 L$.

For case (b),

The argument for case (a) is followed, however the spherical nuclei is allowed to increase linearly with time at rate μ. Nucleation from t_i to t will create a volume increase of

$$dV_t = \frac{4}{3}\pi\kappa^3(t - t_i)^3 u dt_i,$$ ..... (Eq 2.4)

Upon integration of equation 1.3 between $t_i = 0$ and t, and substituted into equation 1.0, one obtains,

$$1 - X = e^{-Kt^4},$$ ..... (Eq 2.5)

where the growth rate, $K = \frac{1}{3}\pi\kappa^3\mu$. By replacing the power of t with Avrami exponent n, the general equation is,

$$1 - X = e^{-Kt^n},$$ ..... (Eq 2.6)

Avrami exponent, n, is the phenomenological index of crystallization, which can be used to discern between different mechanisms of crystallization. For example, when n=1, it corresponds to rod-like growth from instantaneous nuclei ; whereas n=3 or 4 refers to spherulitic growth from either sporadic or instantaneous nucleation. In geopolymer, n

value of 2 and above represents the number of dimensional for the nucleation of crystallization.

Referring to Ismail et al (2007), the degree of crystallinity is first measured by the wax formation on the baffle tube wall, δr, defined as the mass fraction of the wax formed that obtains after cooling process using the Equation 2.2:

$$\delta r = \frac{\delta t - \delta 0}{\delta \infty - \delta 0}$$

δt - deposition at time (min)
δ∞ - maximum or asymptotic deposition from deposition curve
δ0 - initial mass of geopolymer content in liquid (g)

Replacing the X in Equation 6 with δr from Equation 2 and taking log twice for Equation 1.5 it can be written as:

$$\log[-\ln(1 - \delta r)] = logK + nlog(t) \text{ , ...} \quad \text{(Eq 2.7)}$$

The graph can be plotted using the left side as y-axis versus log (t). Then, the straight line slope n and intersection K will be obtain from the graph.
In this study, the degree of crystallinity is measured by the degree of reaction, n of the geopolymer produced by different parameters. By replacing the X in (Eq 2.6) with ε from (Eq 2.9) and taking log twice for (Eq 2.6) it can be written as:

$$\mathbf{\log[-\ln(1 - \varepsilon)] = logK + nlog(t)} \text{ .....} \quad \text{(Eq 2.8)}$$

2.3.2 Degree of Reaction

There are three reactions involve in geopolymerization starting with dissolution, reorientation and solidification. Chemical formulation suggested for geopolymers is :

$$M_n^+\{-(SiO_2)_z - AlO_2 -\}_\varepsilon$$

where M_+ is alkali cation, ε is degree of polymerization and z is the Si/Al ratio (Arioz et al.,2012). Based on his study, degree of reaction is revealed to be increased with increasing concentration. The unreacted fly ash particles existence could be seen by using Scanning Electron Microscope (SEM) which are relatively determined the degree of reaction.

Based on the result reported by Rahman and Kusbiantoro (2014), degree of reaction increased as the sodium nitrate concentration in the mixture is increased. While the addition of citric acid provided a contrast result. The addition of sodium nitrate to increase reaction degree is also parallel to the compressive strength development trend.

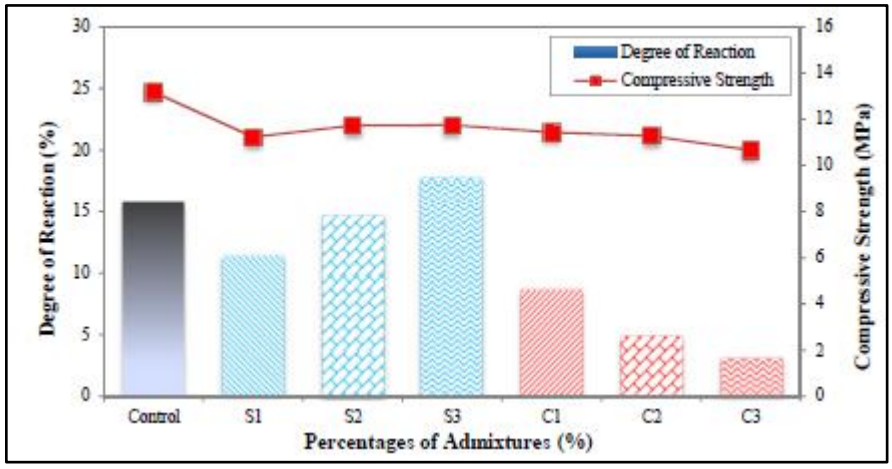

Figure 2.9 Relationship between degree of reaction and compressive strength (Rahman and Kusbiantoro,2014)

The reaction ratio of fly ash was determined by measuring unreacted fly ash using 2 M HCl and 5% Na2CO3 aqueous solution (Sakai et al., 2004). According to Alonso and Palomo (2001), the degree of reaction was calculated by mass difference as follows :

$$\boldsymbol{Degree\ of\ Reaction}, \varepsilon = \frac{m_{sample} - [m_{residue}(1+LOI)]}{m_{sample}} \times 100 \quad \text{..... (Eq 2.9)}$$

where m_{sample} is the weight of powdery sample in g; $m_{residue}$ is the weight of dried residue in g; and LOI stands for the loss of ignition of ground geopolymer paste tested by using X-Ray Fluorescence (XRF).

The amount of unreacted fly ash particles in geopolymer system will increase with lower reactivity of soluble silicate that prevent further dissolution of Al precursors and it will diminish the strength development of hardened specimens. Degree of reaction , ε, values is used to replace cristall volume fraction, x, used in the previous study to study the kineticss of geopolymerization using Avrami's theory.

CHAPTER 3 : METHODOLOGY

3.1 Research Methodology

The research methodology of this study is divided into four main stages which are the preparation of raw materials (fly ash) and alkaline solutions (NaOH, KOH and Na_2SiO_3), characterization of raw materials and alkaline solutions and properties analysis of geopolymer in fresh paste and cured paste respectively. The simplified methodology is presented in Figure 3.1.

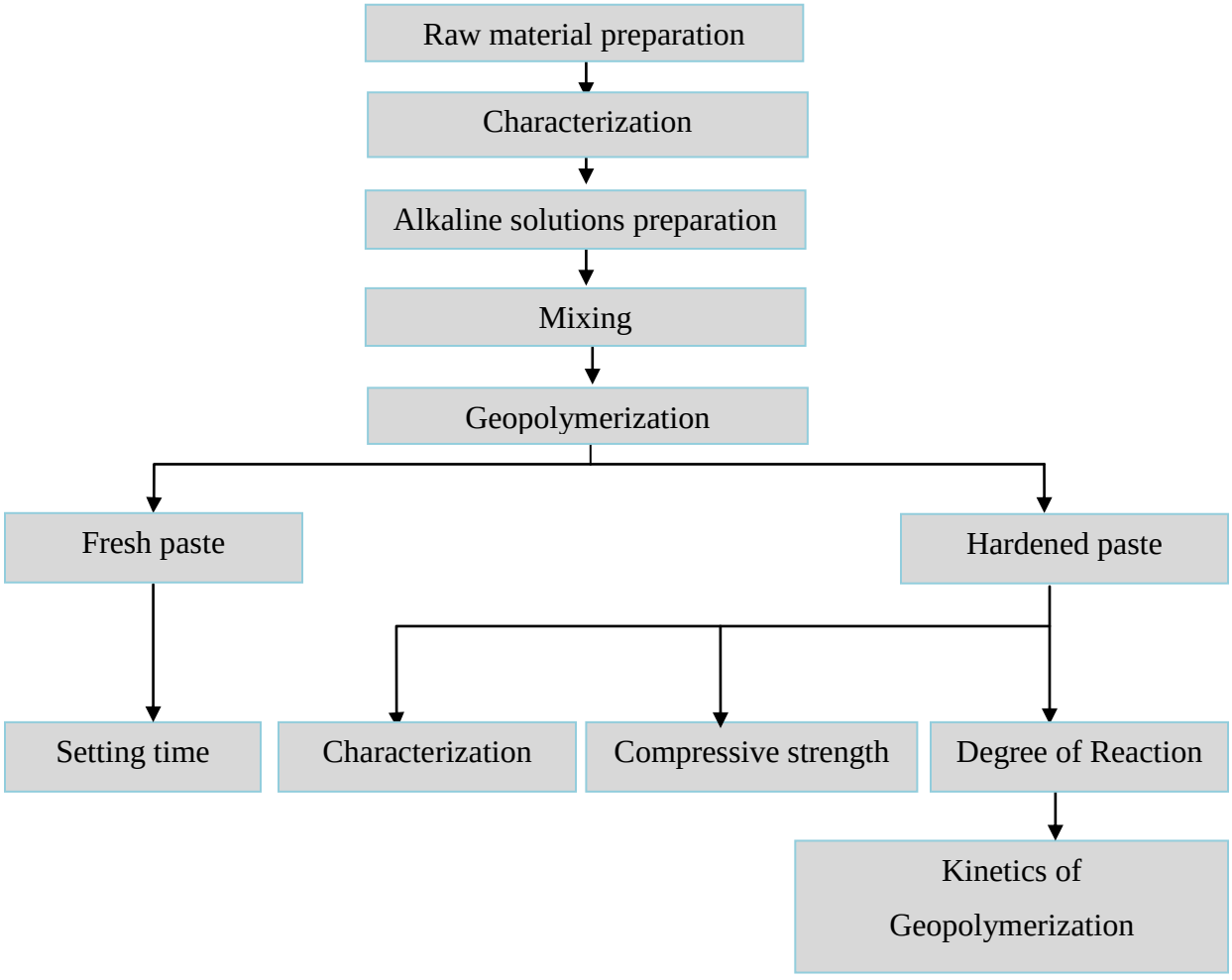

Figure 3. 1 Research methodology of the study

3.2 Raw Material and Alkaline Solutions Preparation

The raw material used for geopolymerization is fly ash. Fly ash is the source for Al and Si for geopolymerization.

The alkaline solutions used for geopolymerization were sodium hydroxide (NaOH), Potassium hydroxide (KOH) and sodium silicate (Na_2SiO_3) (Table 3.1).

Table 3. 1 Preparation of solutions

Solutions	Description
Sodium hydroxide (NaOH)	• Act as dissolver to liberate Al and Si ions for geopolymerization • The NaOH is prepared with molarity of 10 M by dissolving calculated amount of NaOH pellets in distilled water.
Sodium silicate (Na_2SiO_3)	• Act as the binder for the geopolymerization • Pure Na_2SiO_3 is used for geopolymerization

3.3 Characterizations of Raw Material and Geopolymer

After preparing the raw material and alkaline solutions required for geopolymerization, the characteristics of raw materials such as chemical composition and component structure were determined. The raw material was dried up before characterization. Besides that, cured geopolymers were characterized as well (Table 3.2).

Table 3. 2 Equipment used for analysis

Equipment	Description
Compression Machine	To determine the compressive strength of specimen
Fourier Transformed Infrared (FTIR) Specterometer	To determine the chemical composition of fly ash and geopolymer.
X-Ray Fluorescene (XRF)	To determine the Loss of Ignition (LOI) of cured paste

3.4 Geopolymerization

The geopolymerization process was conducted with the preparation of the corresponding raw material and alkaline solutions which are fly ash, NaOH and Na_2SiO_3 respectively according to experimental setups. The prepared materials were mixed using a mechanical mixer for 2 minutes. Well-mixed mixture was quickly casted in 50 mm x 50 mm mould, where setting time of the fresh paste was measured and hardened paste was cured for a predetermined period. In this study, there were two sets of experimental setups involved namely, the first and second experimental setup focused on the effect of curing temperature and concentration of alkaline solution respectively.

3.4.1 Synthesis Parameter

During the preparation of geopolymer paste, there were few parameters considered. The type of raw material, type of alkaline solution, concentration of alkaline solution, mixing ratio, curing temperature and curing period were taken into account. This study is focusing on the curing temperature and alkaline concentration. Thus, the other parameters were fixed to be constant.

3.4.1.1 Curing Temperature

Fly ash was activated by using 10 M NaOH. Then Na_2SiO_3 was added into the mixture. Solid to liquid ratio is 2 : 1. Two sets of experiment conducted with curing temperature was set at 60 ºC and 80 ºC . In order to study the kinetics of geopolymerization, the pastes were cured for 1, 7 and 24 hours respectively. The experimental setup as shown in Table 3.3.

3.4.1.2 Alkaline Concentration

Fly ash was then mixed with NaOH and Na_2SiO_3. Solid to liquid ratio was set to be 2 : 1. Two sets of experiment are conducted with NaOH concentrations of 8 M and 10 M . In order to study the kinetics of geopolymerization, the pastes were cured for 1, 7 and 24 hours respectively. The overall experimental setup are presented in Table 3.4.

Table 3. 3 Experimental Mix design

No	NaOH concentration (M)	Curing temperature (°C)	Solid (kg)	Liquid (kg)		Si/Al ratio
			Fly Ash	NaOH	Na_2SiO_3	
1	8.00	60.00	1	0.15	0.35	4
2	8.00	80.00	1	0.15	0.35	4
3	10.00	60.00	1	0.15	0.35	4
4	10.00	80.00	1	0.15	0.35	4

3.5 Fresh Paste

The fresh paste of geopolymer was used to measure the setting time by using Vicat apparatus.

3.5.1 Setting Time Measurement

The setting time for each sample was determined by using Vicat apparatus. A Vicat needle was used to measure the geopolymer setting time. After the paste was mixed, it was poured into the apparatus mould. By recording the time of a 1 mm needle penetration in the softening specimen, the time of a penetration of 25 mm was determined. This is the initial setting time. The final setting time is when the needle unable sink visibly into the paste. Total time taken for the paste to reach it's harden state was measured as setting time.

3.6 Hardened Paste

3.6.1 Compressive Strength

Compressive strength is defined as the capacity of a material to withstand the force applied to it. The material will crush as the force applied reach the limit of the compressive strength. This is the basic strength measurement method to determine the

strength of the specimens. In this study, the changes in compressive strength will be the determined to study the relation with kinetics of geopolymerization.

According to ASTM C109, the compressive strength of geopolymer specimen was measured by the compression machine. Cured geopolymer was placed in between of the upper and lower plate and the safety door was closed for safety purpose. The specimen was compressed until the yield stress is reached. Te result shown in the indicator was recorded.

3.6.2 Degree of Reaction

Ground samples were added to 2M of HCl solution and stirred for 20 minutes at 60°C. Then the samples were filtrated and washed with distilled water followed by acetone. The samples were heated up to 70°C for 2 hours. Dried samples were added to 3% Na_2CO_3 solution and stirred for 20 minutes at 80°C. Filtration, washing and drying steps were again took place. Subsequently, the mass of the unreacted fly ash was determined. Loss of ignition ws determined by using X-ray Fluorescence .The degree of reaction was calculated by Eq 9.

3.6.3 Kinetics of Geopolymerization

Geopolymerization was analyzed by using derived equation of Avrami' theory.

$$\mathbf{log}[-\mathbf{ln}(\mathbf{1}-\ \boldsymbol{X}\ )] = \boldsymbol{logK} + \boldsymbol{nlog}(\boldsymbol{t})$$

By replacing X with degree of reaction value, ε, equation is written as

$$\mathbf{log}[-\mathbf{ln}(\mathbf{1}-\ \varepsilon\ )] = \boldsymbol{logK} + \boldsymbol{nlog}(\boldsymbol{t})$$

The equation is a linear equation, $y = mx + c$, where

$$y = \log[-\ln(1-\varepsilon)]$$

$$x = \log(t)$$

$$m = n$$

$$c = \log K$$

Straight line graph was plotted to determine the slope which equivalent to the Avrami's constant, n value, and the K value which is the inverse log of y-interception. n values signify the crystall shape while K values are the growth rate of geopolymerization.

CHAPTER 4 : RESULTS AND DISCUSSION

4.1 Characterization of Raw Material

Fly ash used is classified as Class F pozzolanic materials according to Table 4.1 and Figure 4.1. The sum of SiO_2, Al_2O_3 and Fe_2O_3 contained is 78.58 %. It satisfies the standard requirement by American Society of Testing and Materials (ASTM) C618 which the content must be at least 70 %.

Table 4. 1 Chemical Composition of Fly Ash

Component	Chemical Composition (Mass %)
SiO_2	44.518
Al_2O_3	22.479
Fe_2O_3	11.584
CaO	9.841
MgO	3.918
C	2.537
K_2O	1.727
SO_3	1.348
TiO_3	0.671
Na_2O	0.504
P_2O_5	0.333
SrO	0.146
BaO	0.101
Cr_2O_3	0.096
MnO	0.092

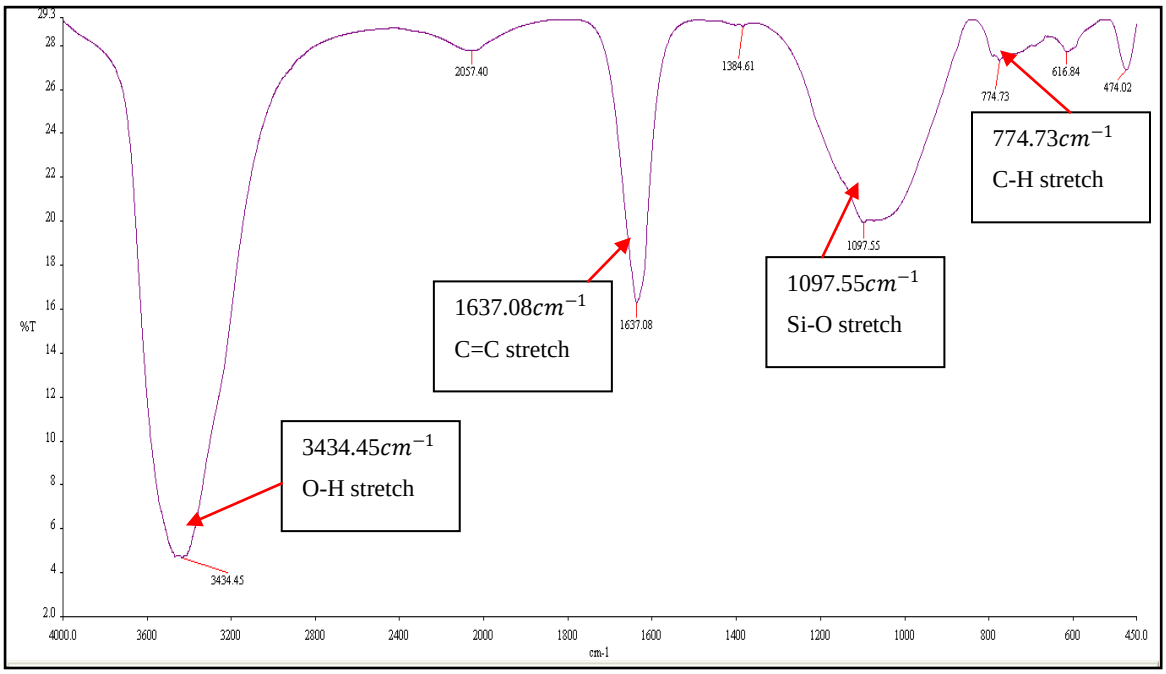

Figure 4. 1 FTIR Analysis of Fly Ash

Particles of fly ash are mostly spherical shape with different size in nature. The particle size distribution shown in Figure 4.2 dictated that the mean particle size of fly ash is 9µm, which is very fine. Smaller size of fly ash particle leads to higher dissolution of raw material with alkaline solutions and give a greater compressive strength.

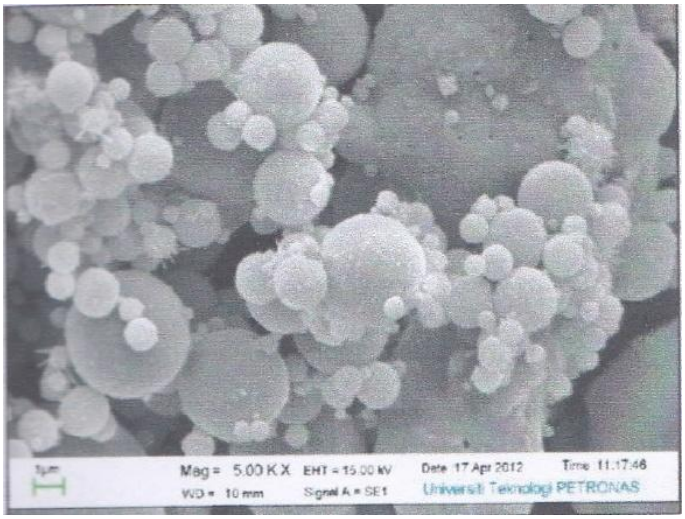

Figure 4. 2 SEM Morphology of Fly Ash

4.2 Experimental Results

The results from experimental works were reported in Table 4.2

Table 4. 2 Experimental Results

No	NaOH conc. (M)	Curing temp. (°C)	Setting Time (min)	Curing Period (hours)					
				1		7		24	
				Comp. Strength (Mpa)	Degree of reaction (%)	Comp. Strength (Mpa)	Degree of reaction (%)	Compressive Strength (Mpa)	Degree of reaction (%)
1	8.0	60.0	190.0	10.56	17.60	35.12	45.11	34.32	60.10
2	8.0	80.0	160.0	10.88	17.70	37.16	47.51	37.20	66.03
3	10.0	60.0	160.0	11.13	21.73	36.27	32.61	37.77	32.06
4	10.0	80.0	160.0	18.51	18.72	38.44	55.94	40.12	56.35

Table 4.2 shows the data recorded through the experimental work. The properties tested were the setting time, compressive strength, and degree of reaction which was further used to study the kinetics of geopolymerization using Avrami's theory. Further discussion of the experimental data are stated in section 4.3, 4.4 and 4.5.

4.3 Physical Properties of Geopolymer

4.3.1 Setting Time

Figure 4.3 shows the setting time of the samples prepared at different concentration of NaOH and curing temperature. The setting time was reduced as higher NaOH concentration was used. It indicated that the setting time was influenced by concentration of hydroxide ions within the mixture. Higher concentration accelerated the reaction rate resulted in shorter setting time. While curing temperature has no effect on the setting time as curing process occurred after the solidification period.

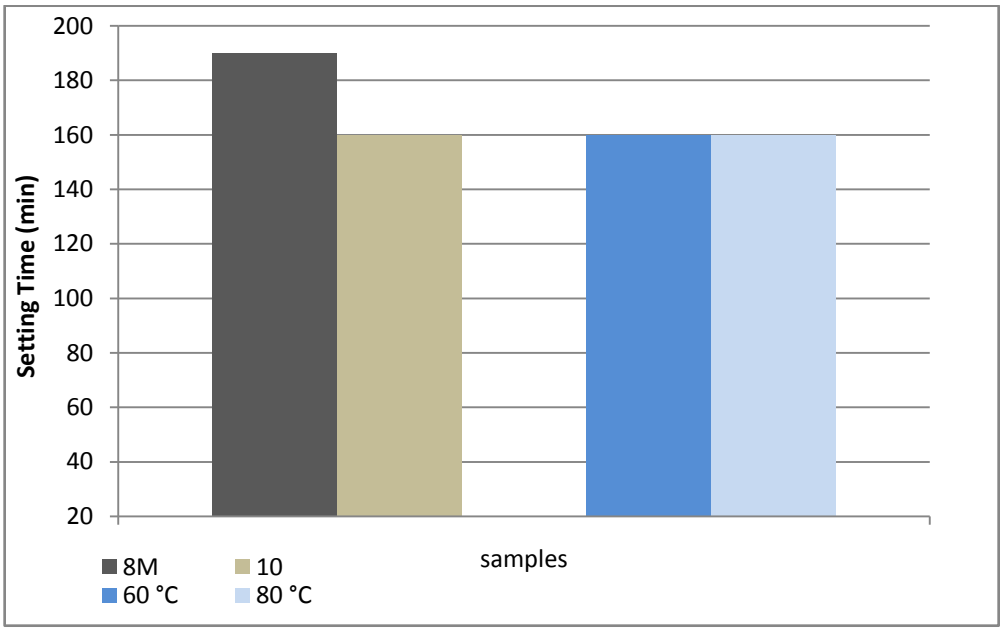

Figure 4. 3 Setting time of samples prepared

4.3.2 Compressive Strength

Figure 4.4 illustrated the effect of NaOH concentration on the compressive strength of geopolymer as a function of curing time. It was observed that compressive strength increased with time. From the figure, the compressive strength of geopolymer with 10 M NaOH was higher than 8 M. It was reported that the use of low alkali solution concentration resulted in a weak chemical reaction. Higher NaOH concentration is more

effective in dissolving fly ash particles to produe geopolymer with high compressive strength.

For 1 hour curing period, the compressive strength of geopolymers showed a significant different between the samples cured at 80 °C and 60 °C. While the samples cured for 7 hours and 24 hours showed a small difference in compressive strength for both condition. The increment in compressive strength was reduced after 7 hours curing period. The result showed that the samples cured at 7 hours were about to reach maximum strength. This is due to the decrement in growth rate as the composition of Si and Al were reduced during geopolymerization.

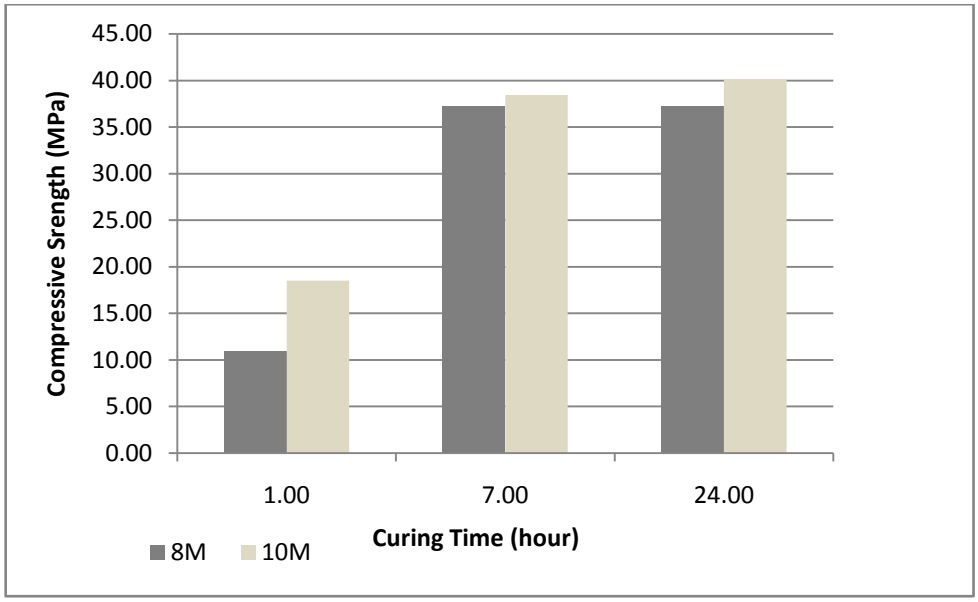

Figure 4. 4 The effect of alkali concentration on the compressive strength

According to Figure 4.5, the compressive strength of geopolymers cured at 80 °C was higher than cured at 60 °C. There was significant increment in compressive strength in between 1 to 7 hours and slight increment between 7 to 24 hours curing period.

The compressive strength of geopolymer increase with time. However the compressive strength of samples cured for 7 hours was similar to the sample cured for 24 hours. At 60 °C, the values were 36.27 and 38.44 MPa for 7 and 24 hours respectively. The result showed that, the samples cured at 7 hours are about to achieve equilibrium state.

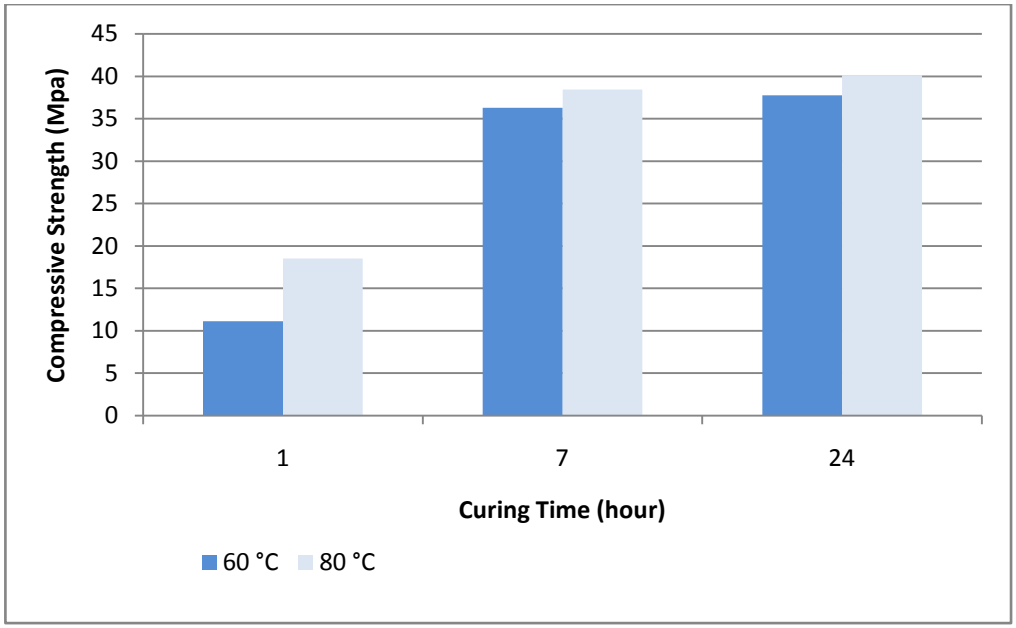

Figure 4. 5 The effect of cring temperature on compressive strength

4.4 Degree of Reaction of Geopolymer

Figure 4.6 shows the effect of NaOH concentration on the reaction degree, ε. The LOI of fly ash was determined to be 1.6 % and been used in determining the ε values. The reaction degree of geopolymers were consistent with the result of compressive strength. The results showed that the degree of reaction increased with increased NaOH concentration. However, the degree of reaction did not show significance increment after 7 hours curing period. Geopolymerization rate was higher during early curing period and slowed down after 7 hours.

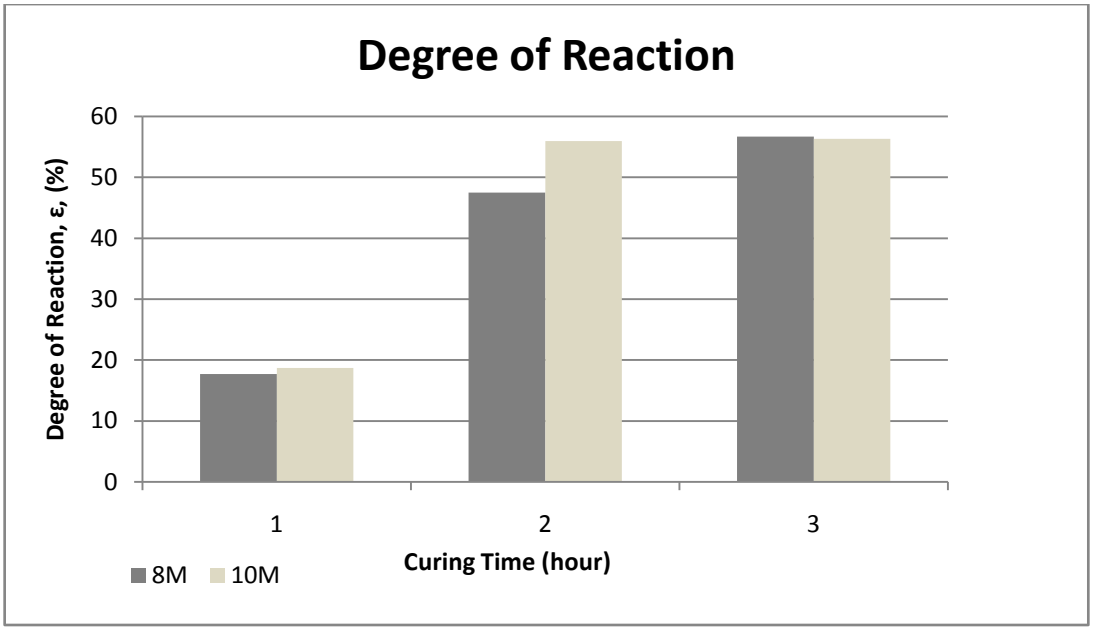

Figure 4. 6 The effect of alkali concentration on degree of reaction

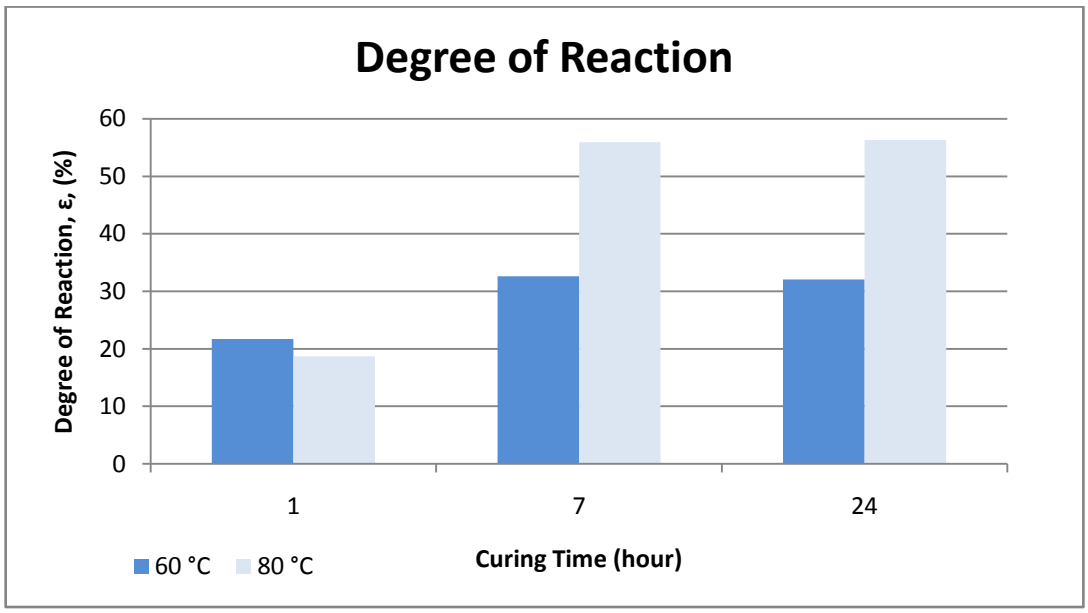

Figure 4. 7 The effect of curing temperature on degree of reaction

The results of the effect of curing temperature on the reaction degree, ε, are shown in Figure 4.7. The highest ε value , 56.35 % was recorded by the sample cured at 80 °C for 24 hours. The reaction degree for samples cured at 80 °C were in line with the result of compressive strength. The results have revealed degree of reaction increased with

increased curing temperature. The degree of reaction pattern was same as the effect of NaOH where there was no significant increment after 7 hours curing period.

4.5 Kinetics of Geopolymerization analysis by using Avrami's Theory

By using the values of reaction degree, ε, the kinetics of geopolymerization could be analyzed using Avrami's theory. Figure 4.8 shows a plot of log (t) versus log |-ln (1-x)| for the effect of NaOH concentration on geopolymerization. From the plot, the Avrami exponent (*n*) and rate constant (K) are determined.

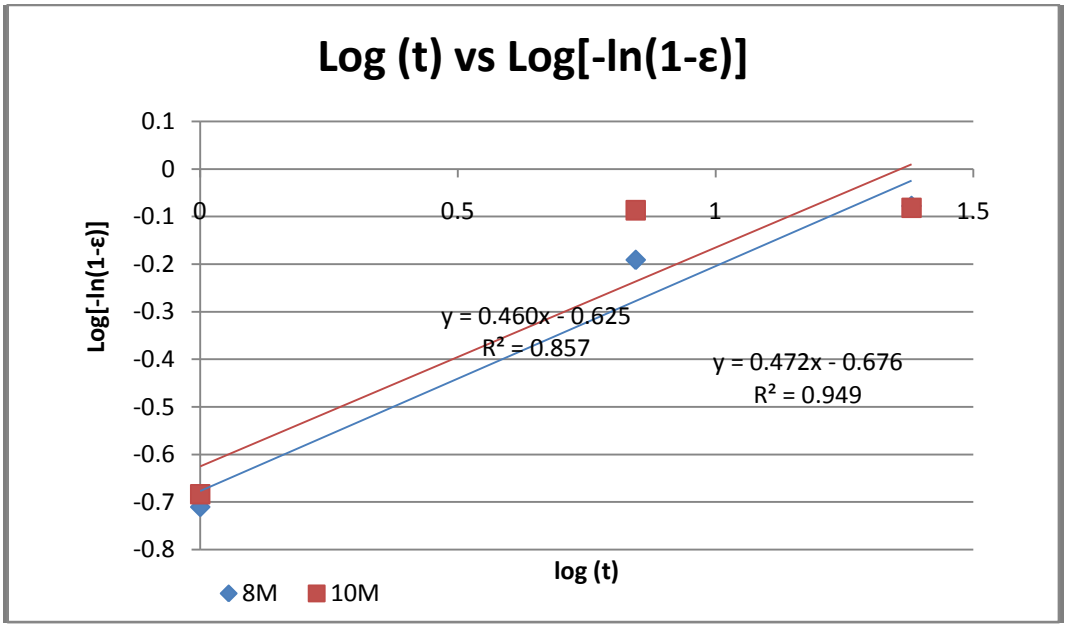

Figure 4. 8 The effect of alkali concentration on kinetics of geopolymerization

Table 4. 3 Extracted Avrami's parameters

NaOH concentration (M)	Avrami's constant (n)	Growth rate (K) (min^{-1})
8	0.472	0.210
10	0.460	0.237

Table 4.3 shows that concentration of NaOH solution slightly affected the value of Avrami's constant (n) and growth rate (K) value. By increasing the concentration of NaOH, the viscosity of the solution was also increased. The mixture with higher

concentration was observed to be more cohesive and reduced the flow ability of the mixture.

Figure 4.9 shows a plot of log (t) versus log |-ln (1-x)| for the effect of curing temperature on geopolymerization. The Avrami exponent (*n*) and rate constant (K) are determined from the straight line plotted.

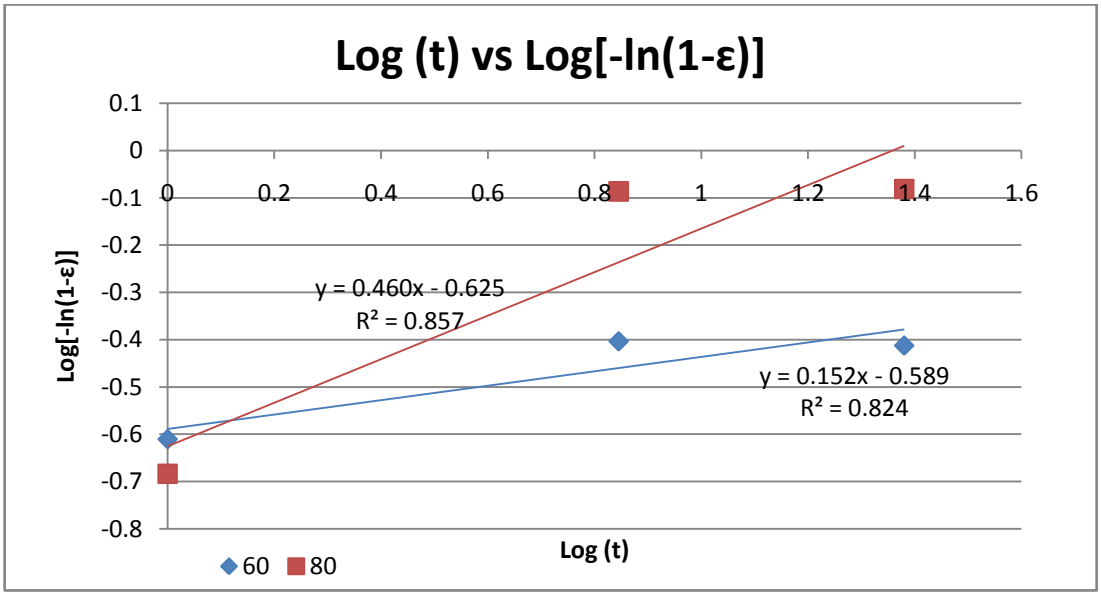

Figure 4. 9 The effect of curing temperature on kinetics of geopolymerization

Table 4. 4 Extracted Avrami parameters

Curing Temperature	Avrami's constant (n)	Growth rate (K) (min^{-1})
60 °C	0.152	0.258
80 °C	0.460	0.237

Based on Table 4.4, the value of Avrami's constant (n) of samples cured at 80 °C was higher than 60 °C. Higher n value signifies that the formation of crystall in geopolymer is better. Crystall formation contributes toward the physical properties of geopolymer such as compressive strength. The results were aligned with the theory that growth rate (K) will decreases the n value increased and vice versa.

CHAPTER 5 : CONCLUSION

5.1 Conclusion

- The setting time was reduced from 190 minutes to 160 minutes as the NaOH was increased from 8M to 10M.
- The compressive strength was increased with the increased of NaOH concentration and curing temperature. After 1 hour curing period, compressive strength increase from 11.13 MPa to 18.51 MPa as the curing temperature was increased from 60 to 80.
- The growth rate (K) slightly increased from 0.51 to 0.54 and crystall shape (n) value slightly decreased from 0.472 to 0.460 with the increased in NaOH concentration from 8 M to 10 M. The K value decreased from 0.258 to 0.237 and n increased from 0.152 to 0.460 as the curing temperature was increased from 60 to 80°C,

RECOMMENDATIONS

For further research of the project, it would be best if a detail study is carried out on the process of geopolymerization. It is suggested that the discussed parameters are measured at wider range to observe the effect on the kinetics of geopolymerization. The addition of samples tested under each parameters discussed would generate more accurate results on the study.

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